

STATE OF CALIFORNIA  
AIR RESOURCES BOARD

AIR MONITORING QUALITY ASSURANCE

VOLUME V

AUDIT PROCEDURES MANUAL

APPENDIX G

PERFORMANCE AUDIT PROCEDURES  
FOR ACID DEPOSITION

MONITORING & LABORATORY DIVISION

NOVEMBER 1996

## APPENDIX G

### PERFORMANCE AUDIT PROCEDURES FOR ACID DEPOSITION

#### TABLE OF CONTENTS

	<u>PAGES</u>	<u>REVISION</u>	<u>DATE</u>
G.1.0 INTRODUCTION	1	1	11-22-96
G.1.0.1 General Discussion of Audit Procedures			
G.2.0 PERFORMANCE AUDIT POLICIES	7	1	11-22-96
G.2.0.1 Responsibility			
G.2.0.2 Policy			
G.2.0.3 Audit Documentation and Forms			
G.2.0.4 Audit Reports			
G.2.0.5 Corrective Actions			
G.3.0 FIELD PERFORMANCE AUDIT PROCEDURES	4	1	11-22-96
G.4.0 LABORATORY PERFORMANCE AUDIT PROCEDURES	3	1	11-22-96
G.5.0 REFERENCES	1	1	11-22-96

## FIGURES

	Page
Figure G.2.0.1. . .California Air Resources Board Acid Deposition Report Form . . . . .	3
Figure G.2.0.2. . .Wet Acid Deposition Performance Audit Preliminary Results Letter . . . . .	4
Figure G.2.0.3. . .Biannual Laboratory Wet Acid Deposition Results . . . . .	5
Figure G.2.0.4. . .Data Validation Screening Tests. . . . .	7
Figure G.3.0.1. . .Field Performance Audit Questionnaire . . . . .	2
Figure G.4.0.1. . .Laboratory Performance Audit Questionnaire . . . . .	2

## **G.1.0 INTRODUCTION**

G.1.0.1 General Discussion of Audit Procedures - Performance audits are used to validate and document the data accuracy of the acid deposition monitoring system. The Quality Assurance Section (QAS) of the Air Resources Board (ARB) conducts both field and laboratory performance audits biannually. The field audits are conducted for pH and the laboratory audits are conducted for pH and conductance. In addition the laboratories also participate in biannual performance surveys that measure the accuracy of ion (nitrate, sulfate, chloride, ammonium, sodium, potassium, calcium, and magnesium) analysis. The following are the general guidelines for ARB performance audits:

1. A performance audit should be conducted only if routine calibrations are being performed.
2. Prior to conducting the audit, a general procedures protocol, that includes the audit policy should be provided to the agency to be audited.
3. The audit will be performed by mail. The auditor will mail the preliminary results to the agency representative. If the agency disagrees with the preliminary results, the auditor should be contacted prior to the release of the final audit results.
4. A signed acknowledgment that the audit has been completed should be obtained from the agency representative.
5. All audit equipment and standards should be referenced to National Institute of Standards and Technology (NIST).
6. The auditor should verify the calibration and traceability of the equipment. A written record of the audit should be kept in a bound notebook.

The auditor should have on file the following information for all sites audited: the address, operating agency, type of instrument being audited, type of calibration used, and general operating procedures. This information may be used later to determine the cause of discrepancies between the audit concentrations and reported responses.

## **G.2.0 PERFORMANCE AUDIT POLICIES**

G.2.0.1 Responsibility - QAS is responsible for preparing and implementing audit procedures. The auditors shall be QAS staff and shall work independently of the operator/analyst functions of the ARB's air quality surveillance and laboratory programs.

### **G.2.0.2 Policy**

1. The audit sample will be mailed to the representative of the air monitoring or laboratory organization. The representative will provide the information required in (a) and (b) below, on the MLD-17A report form (Figure G.2.0.1) supplied with the audit sample.
  - a. Analyzer/sampler make, model, and identification number.
  - b. Analyzer response to audit sample as read from the primary data recording device. Prior to finalizing the audit results, the preliminary audit results shall be verified by the appropriate air monitoring or laboratory supervisor.
2. The operating agency audited is responsible for correcting deficiencies found during an audit.
3. The QAS shall calculate and report data accuracy estimates. Procedures for calculating and reporting data accuracy estimates are presented in Volume I of the Quality Assurance Manual.
4. Instrument adjustments will not be made. If instrument repairs are required, the auditors will postpone the audit until repairs can be made.

### **G.2.0.3 Audit Documentation and Forms**

1. The California Air Resources Board Acid Deposition Sample Report Form, MLD 17A (Figure G.2.0.1) is used by field operators to report audit results.
2. Audit proceedings and results are documented in an audit log book. Audit log books are documented in ink. The log books should include a brief discussion and interpretation of the results together with a discussion of any problem's impact on data integrity and quality. Recommendations should also be included to remedy such problems.

### **G.2.0.4 Audit Reports**

1. Preliminary pH audit results are promptly reported to the sites. (See Figure G.2.0.2)
2. pH, conductivity and ion analysis audit results are promptly reported to the laboratories. (See Figure G.2.0.3)

3. Annually, audit results are reported showing individual and pooled data accuracy estimates. These results are calculated in accordance with the Environmental Protection Agency's (EPA) Quality Assurance Handbook for Air Pollution Systems (Volume V -Precipitation Measurement Systems).

G.2.0.5 Corrective Actions - Whenever an audit indicates an instrument's response deviates from the established control limits, the auditor shall initiate an Air Quality Data Action (AQDA) request to withhold data from entering the ARB's data files until investigation and necessary corrective actions are taken and reported. If necessary, the data are corrected. If data corrections cannot be made, the data shall be invalidated back to the initial occurrence of the malfunction. If the date and time of the malfunction cannot be verified, data shall be invalidated back to the last successful calibration or audit. pH and conductivity control limits are established based on the Data Validation Screening Tests (Figure G.2.0.4). Ion analysis control limits are based on vendor certified acceptance limits and /or  $\pm 20\%$  from true values, whichever is greater.

CALIFORNIA AIR RESOURCES BOARD  
 ACID DEPOSITION SAMPLE REPORT FORM

Station Name \_\_\_\_\_ Reporting Agency \_\_\_\_\_

Observed By \_\_\_\_\_ Date \_\_\_\_\_

County \_\_\_\_\_ Site \_\_\_\_\_ Agency \_\_\_\_\_ Project \_\_\_\_\_

Deposition Type \_\_\_\_\_ Sampling Interval \_\_\_\_\_ Action \_\_\_\_\_ Remark \_\_\_\_\_

Month \_\_\_\_\_ Day \_\_\_\_\_ Year \_\_\_\_\_ 0000-2400  
 Start \_\_\_\_\_  
 Stop \_\_\_\_\_

Field Observation

Rain Gauge

	Tues	Wed	Thurs	Fri	Sat	Sun	Mon	Tues
Type								
Amount (ins)	.	.	.	.	.	.	.	.

Total Precipitation, Rain Gauge (inches): \_\_\_\_\_

Bucket Measurements: \_\_\_\_\_ milliliters or \_\_\_\_\_ grams

Bucket Volume \_\_\_\_\_ Inch Equivalent (Volume x 0.0006): \_\_\_\_\_

Conductance (μS/cm):

Cond. Check Sample: \_\_\_\_\_ Cond. Sample: \_\_\_\_\_

Cond. Distilled Water: \_\_\_\_\_

pH:

pH Check Sample: \_\_\_\_\_ pH Sample: \_\_\_\_\_

Temperature Measurements: Check: \_\_\_\_\_ Sample: \_\_\_\_\_

Analyzed By: \_\_\_\_\_ Date: \_\_\_\_\_

Reviewed By: \_\_\_\_\_ Date: \_\_\_\_\_

Refer to Remark Codes on back.

Other: \_\_\_\_\_

Supply Requests: \_\_\_\_\_

WHITE: MLD LABORATORY PINK: STATION OPERATOR



**Cal/EPA**

California  
Environmental  
Protection  
Agency



**Air Resources Board**

P.O. Box 2815  
2020 L Street  
Sacramento, CA  
95812-2815

MEMORANDUM



Pete Wilson  
Governor

James M. Strock  
Secretary for  
Environmental  
Protection

TO:

FROM: Tracey Vardas, Associate Air Pollution Specialist  
Quality Assurance Section

DATE: November 1, 1996

SUBJECT: PRELIMINARY RESULT OF THE OCTOBER 1996 WET ACID  
DEPOSITION PERFORMANCE AUDIT

The preliminary result of the October 1996 wet acid deposition performance audit has been received and is listed below:

<u>Sample Number</u>	<u>Expected Value</u>	<u>Reported Value</u>
715	4.02	3.94

The attached data validation screening test was used to assess the reported and expected results. Since the expected pH was less than or equal to 5.0, data validation screening test 2.a applies. The difference between the reported and expected pH should be less than 0.2 pH units

If the reported value does not meet the above criteria, a reanalysis sample will be sent to you to verify that the original measurement was not the result of a contaminated sample.

Thank you for your participation. Please check your records to confirm the reported value. If you have any questions, please call me at ATSS 8-492-3892.

Attachment

cc: Peter Ouchida  
Alice Westerinen  
Jennifer Hagins

Figure G.2.0.2  
Wet Acid Deposition Performance Audit  
Preliminary Results Letter





**Cal/EPA**

California  
Environmental  
Protection  
Agency



**Air Resources Board**

P.O. Box 2815  
2020 L Street  
Sacramento, CA  
95812-2815

MEMORANDUM

TO: Qingqing Lu, ARE  
Inorganics Laboratory Section

FROM: Tracey Vardas, Associate APS  
Quality Assurance Section

DATE: October 28, 1996

SUBJECT: BIENNIAL LABORATORY WET ACID DEPOSITION RESULTS



Pete Wilson  
Governor

James M. Strock  
Secretary for  
Environmental  
Protection

Thank you for participating in the Quality Assurance Section's (QAS) Fall 1996 laboratory wet acid deposition performance audit. Attached is a copy of the audit results. The results include a comparison between the laboratory's reported values and the QAS's expected values. The results indicate that the laboratory is operating within the U.S. Environmental Protection Agency's (U.S. EPA) control limits.

The audit was conducted in accordance with the U.S. EPA's Quality Assurance Handbook for Air Pollution Systems (Volume V - Precipitation Measurement Systems). If you have any questions or comments concerning these results, please contact me at 322-3892.

Attachment

cc: George Lew  
Alice Westerinen  
Chas Cowell  
Jennifer Hagins

**Results of the Biannual  
Wet Acid Deposition Laboratory Audit  
OCTOBER 1996**

Sample Number 6400

Analyte	Units	Reported Values	Expected Values	Difference	Percent Difference *
pH	pH	4.02	4.03	-0.01	-0.2
Conductance	uS/cm	59.3	68.5	-9.20	-13.4
SO4	mg/L	5.649	5.700	-0.051	-0.9
NH4	mg/L	0.538	0.533	0.005	0.9
NO3	mg/L	2.764	2.850	-0.086	-3.0
Cl	mg/L	1.101	1.120	-0.019	-1.7
Ca	mg/L	0.120	0.113	0.007	6.2
K	mg/L	0.554	0.561	-0.007	-1.2
Mg	mg/L	0.336	0.321	0.015	4.7
Na	mg/L	1.341	1.340	0.001	0.1

\* Percent Difference = (Reported-Expected)/Expected\*100

DATA VALIDATION SCREENING TESTS

Test	Required Action
2. Compare pH measured in the field (FpH) against pH measured in the laboratory (LpH).	
a. If $\text{pH} < 5.0$ and $\text{LpH} - \text{FpH} \geq 0.2$ , flag suspicious data.	a. Repeat laboratory pH measurement. If previous pH is confirmed, remove suspicious flag and accept pH data provided $\text{LpH} - \text{FpH} < 0.7$ . If the difference exceeds 0.7 pH units, both pH data points remain invalid until field remeasurement.
b. If pH is between 5.0 and 9.0 and $\text{LpH} - \text{FpH} > 0.5$ , flag suspicious data.	b. Repeat laboratory pH measurement. If previous pH is confirmed, remove suspicious flag and accept both pH provided $\text{LpH} - \text{FpH} < 1.0$ . If the difference exceeds 1.0 pH unit, both pH data points remain invalid until field remeasurement.
	c. If remaining volume is $> 100$ ml and both LpH and FpH remain invalid and field and lab pH check samples are equal to $\pm 0.15$ pH of standard value confirm field measurement by shipping sample to field for remeasurement. If field remeasurement is confirmed remove suspicious flag, accept data and report to AQD Section.
3. Compare conductivity measured in the field (FCond) against conductivity measured in the laboratory (LCond).	
a. If $\text{LCond} < 20$ $\mu\text{mhos/cm}$ and $\text{FCond} - \text{LCond} \geq 5$ $\mu\text{mhos/cm}$ , set suspicious data flag on Cond data.	a. Repeat laboratory conductivity measurement. If previous LCond is confirmed, remove flag provided $(\text{FCond} - \text{LCond}) < 10$ $\mu\text{mhos/cm}$ . If the difference exceeds 10 $\mu\text{mhos/cm}$ both Cond data points remain invalid unless c. applies.
b. If $\text{LCond} > 20$ $\mu\text{mhos/cm}$ and $\left( \frac{\text{FCond} - \text{LCond}}{\text{LCond}} \right) \times 100 \geq 20 \text{ percent}$ set suspicious data flag on Cond data.	b. Repeat laboratory conductivity measurement. If previous conductivity is confirmed, remove flag if the ratio is $< 100$ percent. If the ratio is $> 100$ percent both Cond data points remain invalid unless c. applies.
	c. If remaining sampler volume is $> 100$ ml and both LCond and FCond remain invalid and the conductivity standard is $\pm 10$ percent of standard value confirm field measurement by shipping sample to field for remeasurement. If field remeasurement is confirmed remove suspicious flag, accept and report to AQD Section.

Figure G.2.0.4  
Data Validation Screening Tests

### G.3.0 FIELD PERFORMANCE AUDIT PROCEDURES

A performance audit for a precipitation monitoring network should be made at least twice per year for pH at all sites. These audits will be accomplished by mailing audit samples to the field sites for analysis. A Field Performance Audit Questionnaire (Figure G.3.0.1) will also be sent with the audit sample for completion by the field representative. The completed questionnaire must be returned along with the audit results.

A performance audit will include the following activities:

1. Check Sample Analysis - The auditor supplies a check sample of known pH.
  - a. The operator is asked to treat this sample as though it were a routine precipitation sample.
  - b. Upon return of the audit sample, the results are recorded and an assessment of the accuracy is obtained.
2. Review of Procedures and Data Documentation (based on answers supplied on Field Performance Audit Questionnaire).
  - a. The auditor should review the questionnaire as soon as it is received. This should include reviewing the sections pertaining to handling of samples and sampling containers, quality control checks and adherence to procedures for instrument operation and data recording.
  - b. The auditor should then review the sections on standards information (pH), sample treatment after analysis, water supply and data recording. These sections are used to assess operator training and performance.

Field Performance Audit Questionnaire

Site Name: \_\_\_\_\_ Site Number: \_\_\_\_\_  
Site Address: \_\_\_\_\_ Site Phone: \_\_\_\_\_  
Site Operator: \_\_\_\_\_ Date: \_\_\_\_\_

=====

A. GENERAL

- |   | <u>YES</u> | <u>NO</u> |
|---|------------|-----------|
| 1. Does the operator have a copy of the Field Operations Manual (Volume II, Appendix N)?  | _____      | _____     |
| 2. Does the operator have the instrument manufacturers manual?  | _____      | _____     |
| 3. Does the operator have the necessary spare parts and hand tools to calibrate the rain gauges and pH meter?   | _____      | _____     |
| 4. Is the work space used for sample analysis maintained at 25°C ± 5°C and meet the requirements of cleanliness (possible contamination of chemicals nearby, etc.)? | _____      | _____     |
| 5. Is a refrigerator available to store acid deposition samples?  | _____      | _____     |

B. SITING AND NETWORK DESIGN

- |  |       |       |
|--|-------|-------|
| 1. Has the site been formally reviewed and approved by the QAS?  | _____ | _____ |
| 2. Siting Criteria   |       |       |
| a. Does rain fall at the site unobstructed?  | _____ | _____ |
| b. Are the precipitation collector and rain gauge at least 2 but less than 15 meters apart?                      | _____ | _____ |
| c. Is the rain gauge level?  | _____ | _____ |
| d. Can the rain gauge measure 0.01 inches of precipitation?  | _____ | _____ |
| e. Do the site records contain a copy of completed site report with site number and name approved by QA Section? | _____ | _____ |

Figure G.3.0.1  
Field Performance Audit Questionnaire

	<u>YES</u>	<u>NO</u>
3. Does the network design consider access, power availability and localized interferences?	___	___
4. Are the instruments installed in accordance with the manufacturer's and/or QAS's specifications?	___	___
5. Are the instruments at the site operated in accordance with the standard operating procedures in Volume II, Appendix N?	___	___
6. Does the site maintain an adequate supply of expendables and spare parts to service the instruments on time to minimize loss of data due to malfunctions?	___	___
7. Are necessary precautions taken during winter with the rain gauge and event recorder (antifreeze, funnel removal, heater, etc.)?	___	___
 <b>C. <u>NETWORK MAINTENANCE AND CALIBRATION</u></b>		
1. Is preventative maintenance performed in accordance with Volume II, Appendix N?	___	___
2. Is the collector sensor cleaned periodically?	___	___
3. Is the collector rim of dry bucket wiped clean with damp Kimwipes weekly in a manner that prevents deposits on the rim from falling into the bucket?	___	___
4. Are the rain gauge pens checked weekly for ink?	___	___
5. Are all the instruments calibrated under the same conditions as they are operated?	___	___
6. Are pH meters verified for proper calibration by using standards before samples are measured?	___	___
7. Are records kept documenting all:		
a. Audits?	___	___
b. Calibrations?	___	___
 <b>D. <u>QUALITY CONTROL AND QUALITY ASSURANCE ACTIVITIES</u></b>		
1. Is QC data documented to show acceptability?	___	___
2. Is chain-of-custody documentation maintained for all samples?	___	___
3. Is the pH electrode stored in the proper pH buffer?	___	___

Figure G.3.0.1  
Field Performance Audit Questionnaire (continued)

- |  | <u>YES</u> | <u>NO</u> |
|--|------------|-----------|
| 4. Is the pH electrode rinsed well with distilled/<br>deionized water after removal from the buffer? | _____      | _____     |
| 5. Are samples allowed to come to room temperature<br>before pH is measured?                         | _____      | _____     |
| 6. Are control charts of the field pH check samples<br>recorded?                                     | _____      | _____     |
| 7. Are the control charts checked to verify that<br>the results are in control?                      | _____      | _____     |

E. DATA HANDLING PROCEDURES

- |   |       |       |
|---|-------|-------|
| 1. Are the site data record sheets made for each<br>sample?                         | _____ | _____ |
| 2. Is one copy of the data sheet kept for each<br>sample?                           | _____ | _____ |
| 3. Is a log book maintained?  | _____ | _____ |
| 4. Are problems, equipment changes, standards,<br>etc., documented in the log book? | _____ | _____ |

#### G.4.0 LABORATORY PERFORMANCE AUDIT PROCEDURES

A laboratory performance audit for a precipitation monitoring network should be made at least twice per year for pH, conductance and ion analysis. These audits will be accomplished by mailing audit samples to the laboratory for analysis. A Laboratory Performance Audit Questionnaire (Figure G.4.0.1) will also be sent with the audit sample for completion by the laboratory representative. The completed questionnaire must be returned with the audit results.

A laboratory performance audit for pH, conductance and ion analysis will include the following activities:

1. Check sample analysis - The auditor supplies a check sample of known pH, conductance and ion concentration.
  - a. The representative is asked to treat this audit sample as though it were a routine precipitation sample.
  - b. Upon return of the audit the results are recorded and an assessment of the accuracy is obtained.
2. Review of Procedures and Data Documentation (based on answers supplied on Laboratory Performance Audit Questionnaire).
  - a. The auditor should review the questionnaire as soon as it is received. This should include reviewing the sections pertaining to handling of samples and sampling containers, quality control checks and adherence to procedures for instrument operation and data recording.
  - b. The auditor should then review the sections on standards information, sample treatment after analysis, water supply, and data recording. These sections are used to assess operator training and performance.



Laboratory Performance Audit Questionnaire

Laboratory Name: \_\_\_\_\_ Number: \_\_\_\_\_

Address: \_\_\_\_\_ Phone: \_\_\_\_\_

Operator: \_\_\_\_\_ Date: \_\_\_\_\_

=====

A. <u>GENERAL</u>	<u>YES</u>	<u>NO</u>
1. Does the operator have a copy of the Laboratory's Standard Operating Procedures (SOP)?	_____	_____
2. Does the operator have the instrument manufacturer's manuals?	_____	_____
3. Does the operator have the necessary spare parts and hand tools to calibrate the pH meter, conductivity meter, and ion analysis instrumentation?	_____	_____
4. Is the space used for sample analysis maintained at 25°C ± 5°C and meet the requirements of cleanliness (possible contamination of chemicals nearby, etc.)?	_____	_____
5. Is a refrigerator available to store acid deposition samples?	_____	_____
 B. <u>NETWORK MAINTENANCE AND CALIBRATION</u>		
1. Is preventative maintenance performed in accordance with the SOP'S?	_____	_____
2. Is the calibration schedule followed as indicated in the SOP?	_____	_____
3. Are all the instruments calibrated under the same conditions as they are operated?	_____	_____
4. Are all the instruments calibrated before sample measurements?	_____	_____
5. Are records kept documenting all:		
a. Audits?	_____	_____
b. Calibrations?	_____	_____

Figure G.4.0.1  
Laboratory Performance Audit Questionnaire

		<u>YES</u>	<u>NO</u>
C.	<u>QUALITY CONTROL AND QUALITY ASSURANCE ACTIVITIES</u>		
1.	Is the QC data documented to show acceptability?	___	___
2.	Is chain-of-custody documentation maintained for all samples?	___	___
3.	Is the pH electrode stored in the proper pH buffer?	___	___
4.	Is the pH electrode rinsed well with distilled/deionized water after removal from the buffer?	___	___
5.	Are samples allowed to come to room temperature before measurements?	___	___
6.	Is the conductivity of the rinse water measured and recorded?	___	___
7.	Are the control charts of pH and conductivity check samples recorded in the laboratory?	___	___
8.	Are the control charts checked to verify that the results are in control?	___	___
D.	<u>DATA HANDLING PROCEDURES</u>		
1.	Are data record sheets made for each sample?	___	___
2.	Is one copy of the data sheet kept for each sample?	___	___
3.	Is a log book maintained?	___	___
4.	Are problems, equipment changes, standards, etc., documented in the log book?	___	___
5.	Are duplicate samples identified properly?	___	___

#### G.5.0 REFERENCES

1. Quality Assurance Manual, Volume V, Audit Procedures Manual.
2. Quality Assurance Handbook for Air Pollution Measurement Systems: Volume II, Ambient Air Specific Methods, Section 2.0.12, U.S.E.P.A., September 1985.
3. Quality Assurance Manual for Precipitation Measurement Systems Environmental Monitoring Systems Laboratory, U.S. E.P.A., Revised January 1985.
4. NADP Quality Assurance Plan, Deposition Monitoring, NADP Quality Assurance Steering Committee, 1984.